# Thermal Elasticity in Glassy Alloys based on Topology of Metallic Clusters



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# Thermal Elasticity in Glassy Alloys based on Topology of Metallic Clusters

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Thermal elasticity of two kinds of bonding-type glassy alloys, $Zr_{55}Cu_{30}Al_{10}Ni_5$ and $Pd_{40}Cu_{30}Ni_{10}P_{20}$, during progressive devitrification was evaluated by Poisson's ratio, Debye temperature, and internal frictions in terms of topological change in metallic clusters. Both alloys showed opposite behavior for thermal elasticity: thermal softening associated with relaxation of icosahedral clusters and thermal-induced entropy elasticity associated with the rotational and vibrational motions of polyhedral clusters, and an increment of internal friction based on electron-longitudinal phonon interaction derived from the variation amount of potential energy among atoms, showing vanishment of free electrons. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2803068]

Bulk glassy alloys can be regarded as the last frontier of metals and metallic alloys. Much attention has been devoted to the glass forming ability of different types of alloy systems in glassy alloys,[1] i.e., their cluster structures[2] and their potential applications. The distinguishing feature of glassy alloys without crystal structure is attributed to the randomness of their potential energy.[1] The potential energy minimum among atoms in the multicomponent bulk metallic glasses is not as rigid as that of crystal alloys, so that the wave functions of these electrons are irregularly spread out much more in space than those of the crystalline metallic valence electrons. Furthermore, glassy alloys have metal/metal and metal/metalloid bonding types,[3] and the atomic configurations of the glassy alloys differ among their two bonding-type alloys. The glassy structure of the former is composed of icosahedral clusters [inset (a) of Fig. 3], while the structural feature of the alloy of the latter is the construction of network atomic configurations consisting of trigonal prisms [inset (b) of Fig. 3][4] and transformed tetragonal dodecahedrons.[2] Therefore, there is a possibility that thermal behaviors of metallic clusters during progressive devitrification are different between the two kinds of glassy alloys.

In a previous paper,[5] we reported that a $Pd_{40}Cu_{30}Ni_{10}P_{20}$ glassy alloy with high glass-forming ability and high stability of supercooled liquid showed a rubberlike entropy elasticity below the second-order-like phase transition at 500 K, from observations of thermal-induced entropy elasticity by ultrasonic measurements and the Gough-Joule effect.[6] The glassy alloy is a representative one, characterized by metal/metalloid bonding-type. The elasticity has been explained by thermal dynamic micro-Brownian stretching, described as $F(\mathrm{Pa})=0.282T+562$, which is associated with the rotational and vibrational motions of polyhedral clusters (inset of Fig. 1)[7] or locally collective atomic motion, which corresponds to a hingelike motion between trigonal prismatic structure units connected by shearing edges.[8] On the other hand, a $Zr_{55}Cu_{30}Al_{10}Ni_5$ alloy, which is a typical alloy consisting of metal/metal bonding-type, has high thermal stability.[9]

Our interest lies in studying thermal elasticity of two kinds of bonding-type glassy alloys, $Zr_{55}Cu_{30}Al_{10}Ni_5$ and $Pd_{40}Cu_{30}Ni_{10}P_{20}$, during progressive devitrification in terms of topological change in metallic clusters. Longitudinal and transverse wave velocities and dilational and shear internal frictions of the glassy alloys have been simultaneously measured as a function of temperature ranging from 298 to 673 K. Since the longitudinal wave interacts with electrons and the transverse one lacks such interactions,[10] simultaneous measurement provides much useful information about structural changes, phase-transition order, and elastic and electronic contributions for glassy alloys. As far as we know, however, no research work has been carried out previously on measurement of elastic parameters and internal frictions for the glassy alloys, using both longitudinal and transverse wave velocities with the same frequency.

The specimens (density of 9.285 $\mathrm{Mg/m^3}$ and $T_g=560$ K for $Zr_{55}Cu_{30}Al_{10}Ni_5$, and density of 6.829 $\mathrm{Mg/m^3}$ and $T_g=690$ K for $Pd_{40}Cu_{30}Ni_{10}P_{20}$), produced by an injection casting method[9] was in the form of a long rod (10 mm in diameter and 8 mm in length) fastened to a stainless steel waveguide with threads of pitch of 1.5 mm, using a domed cap nut made of stainless steel. Naphtenic hydrogen oil with a viscosity of 400 Pa s was used as a couplant medium between the specimen and the waveguide, to improve nonequilibrium of heat distribution for the sample in a previous paper.[11] We used a longitudinal wave generation PZT $[\mathrm{Pb}(\mathrm{Zr}_x\mathrm{Ti}_{(1-x)})3]$ transducer with 7 MHz frequency as an optimum frequency. The specimen was measured from 298 up

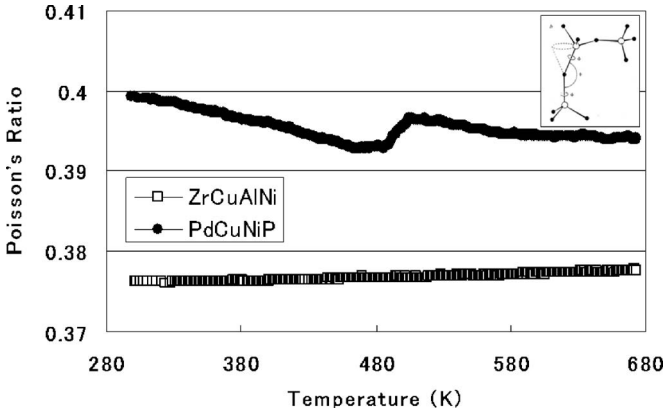


FIG. 1. Temperature dependence of Poisson's ratio for glassy alloys $Zr_{55}Cu_{30}Al_{10}Ni_5$ and $Pd_{40}Cu_{30}Ni_{10}P_{20}$. Inset: rotation about bonds in medium-range order cluster.

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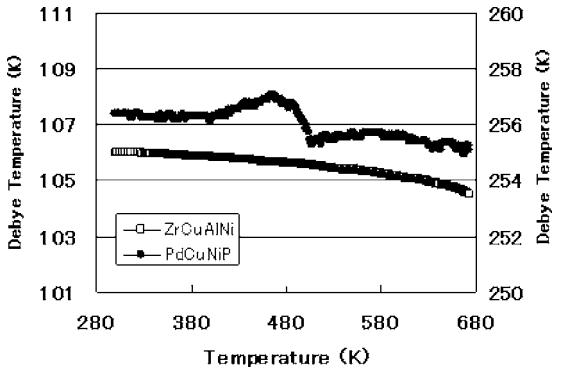


FIG. 2. Temperature dependence of elastic Debye temperature for glassy alloys $Zr_{55}Cu_{30}Al_{10}Ni_5$ and $Pd_{40}Cu_{30}Ni_{10}P_{20}$.

to 673 K at a heating rate of 0.03 K/s in an argon atmosphere at an ambient pressure. The difference between the top and the bottom of the specimen was ±0.5 K during measurement. The experimental procedure is described in a previous paper.[12] For the calculation of Debye temperature,[13] we used 3.45 and 4 as the number of degree of freedom and $1.103\times10^{-27}$ and $5.06\times10^{-29}$ $m^3$ as an average atomic volume for $Zr_{55}Cu_{30}Al_{10}Ni_5$ and $Pd_{40}Cu_{30}Ni_{10}P_{20}$, respectively. Increasing and decreasing rates in the internal friction, $Q^{-1}$ and $Q^{-s}$, at temperature $T$ of longitudinal and transverse waves, respectively, were calculated using the ratio of the logarithmic echo amplitude of the ultrasonic pulse wave at given temperatures to the corresponding amplitude measured at the lowest temperature.[5,12]

Since the directional property of Poisson's ratio is designated by the quotient of lateral to longitudinal strain $e_{ij}=-S_{ij}/S_{ij}$ ($i$, and $j=1$, 2, and 3) (where $S_{ij}$ stands for the elastic compliance constants) for all possible orientations of the coordinate system, we evaluate Poisson's ratio from three-dimensional volume-nonpreserving elastic deformability of view. The changes in Poisson's ratio are of great interest as these directly affect the mechanical properties such as ductility/toughness.[14,15] Temperature dependence of Poisson's ratio for two alloys is shown in Fig. 1. Poisson's ratio of $Zr_{55}Cu_{30}Al_{10}Ni_5$ increases gradually with increasing temperature, showing thermal softening similar to that for general materials. This could be derived from the relaxation of icosahedral clusters [inset (a) of Fig. 3].[16,17] By striking contrast, the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ shows wholly a decrease except for a jump at around 500 K, based on enthalpy elasticity by the vibration of trigonal prism caped with the half octahedral [inset (b) of Fig. 3], showing an enhancement of toughness in the volume-nonpreserving distortion.[5] Lewandowski *et al.*[15] have also reported that the Pd based glassy alloys are significantly tougher than the Zr based ones, consistent with the higher Poisson's ratio of the former.

To investigate an effect of atomic movement for both alloys, we next show the temperature dependence of elastic Debye temperature for both alloys in Fig. 2. Negligible change with a temperature variation of ±1.0 K in both alloys indicates negligible tiny change in the effective atomic distance for the devitrification. Thus, we must consider topological change of metallic clusters in place of atomic modification for the contrary result in Fig. 1.

Internal friction is a property which depends on the nonideal elastic behavior (anelasticity), which yields information about various stages of incipient crystallization such as strain

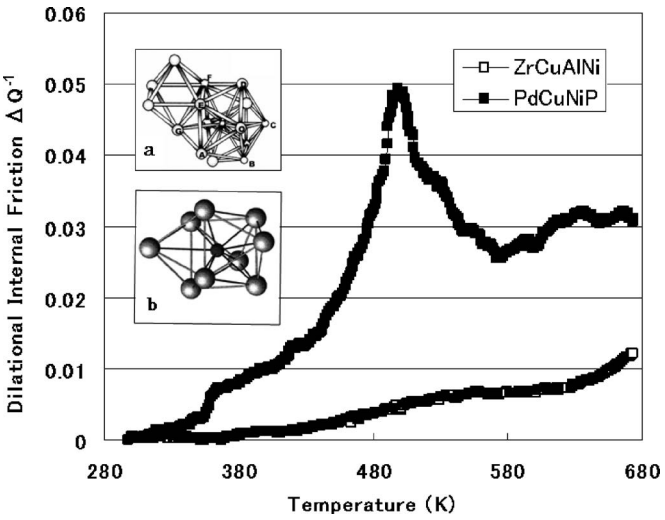


FIG. 3. Temperature dependence of dilational internal friction for glassy alloys $Zr_{55}Cu_{30}Al_{10}Ni_5$ and $Pd_{40}Cu_{30}Ni_{10}P_{20}$. Insets: (a) trigonal prism cluster caped with three half octahedral; (b) icosahedron cluster.

relief,[18] softening,[19] embryo nucleation,[18] and micro-Brownian motion.[20] Internal dilational friction curves for both glassy alloys are shown in Fig. 3, as a function of temperature. The dilational friction of the $Zr_{55}Cu_{30}Al_{10}Ni_5$ gradually increases, while the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ shows one large peak at 500 K on the background curve which monotonically rises with increasing temperature. The slope of the latter is about three times larger than that of the former. The 500 K peak was related to interatomic readjustment associated with atomic rotation underlying relaxation process in the previous paper.[5] Assumed from physical meanings of the dilational friction,[21,22] the notable increment of the friction for both alloys could be raised from electron-longitudinal phonon interaction associated with the variation amount of potential energy among atoms. In other words, the noticeable increase of the interaction means a vanishment of many free electrons during progressive crystallization. Here, it should be noted that the electron valences of the constituent elements of the glassy alloys are somewhat larger (~7.2) than those (~6) predicted by crystalline metallic valence bond theory, showing a valence electron contribution (VEC) associated with *spd or spf* hybridization for glass formation.[23] For corroborated evidence for the noticeable increment of the latter, indeed, VEC (4.825) of the former is lower than that (5.96) of the latter.

The temperature dependence of the internal shear frictions for both alloys is presented in Fig. 4. The shear curve of the $Zr_{55}Cu_{30}Al_{10}Ni_5$ shows one tiny peak at 510 K on the decreasing curve line, while the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ peak reveals a single deep valley (an abrupt drop from 440 K and a subsequent rapid rise from 500 K). For the 510 K peak, we cannot make any assignment at the present time. The drop of the latter is derived from an accumulation of strain, and the subsequent rapid increase comes from crystallization, as deduced from the physics of shear friction.[5,11,12,18–20] Thus, the shear friction does not provide important information on thermal elasticity.

Since both alloys are characterized by the topological change in metallic clusters accompanied by large vanishment of free electrons, we lastly consider an electronic contribution for the progressive devitrification in terms of bonding

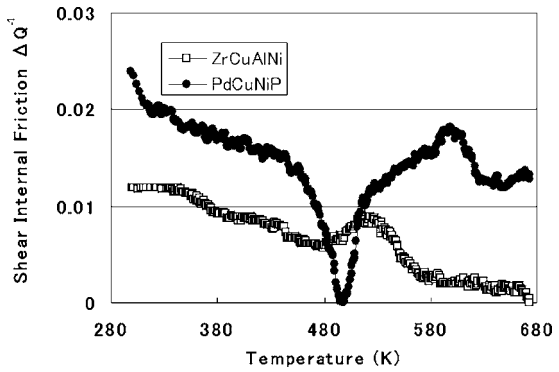


FIG. 4. Temperature dependence of shear internal friction for glassy alloys $Zr_{55}Cu_{30}Al_{10}Ni_5$ and $Pd_{40}Cu_{30}Ni_{10}P_{20}$.

character in metallic clusters, using their temperature dependent compressibility data. Since outer electrons in the glassy alloy are not settled in electronic structure with discrete permitted energies, many free electrons can move around random metal cations in the glassy alloys. According to ideal gas model, the pressure of the material arises almost entirely from the electrons, both because they outnumber the nuclei and because of their smaller mass.[24] In electronic kinetic theory the relation between electronic pressure $P$ and the total number of electrons per unit volume $n$ is given by

$$P = \frac{1}{5}\left(\frac{3}{8\pi}\right)^{2/3}\frac{h^2}{m}n^{5/3}. \quad (1)$$

Since the number $n$ is related to the effective potential energy $U$ of outer electrons by the formula,

$$n = \frac{8\pi}{3h^3}(-2mU)^{3/2}. \quad (2)$$

Combining Eqs. (1) and (2) gives

$$P = \frac{8\pi}{15h^3}m^{3/2}(-2U)^{5/2}, \quad (3)$$

where $h$ is the Plank constant and $m$ is the mass of electron. Thus, we can calculate the effective potential energy $U$ of the free electrons for the glassy alloys of interest, using the thermal dynamic force $F$. The result is presented in Fig. 5. An increase in temperature indicates a decrease in the potential energy, especially for $Pd_{40}Cu_{30}Ni_{10}P_{20}$, that is, stabilization of electronic system during progressive devitrification.

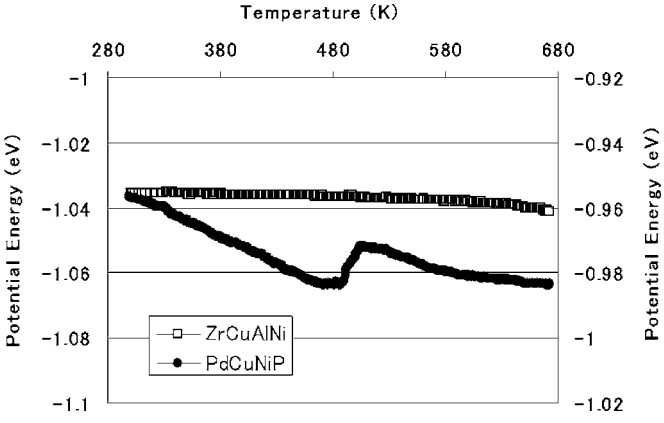


FIG. 5. Temperature dependence of the effective potential energy for glassy alloy $Pd_{40}Cu_{30}Ni_{10}P_{20}$ in thermoelastic effect.

In this study, we assumed that many free electrons move around in the glassy alloys. Such an interelectron Coulomb interaction does not contribute to a self-consistent field; this direct interaction leads to a cooperative electron motion (i.e., collective resonances), associated with many electrons in heavy atoms analogous to hydrodynamic or sound vibrations.[25] It is known that the total oscillator strength in the collective resonance is approximately equal to the total number of oscillating electrons;[26] for $Pd_{40}Cu_{30}Ni_{10}P_{20}$, it is ~10 for the $3d$ and $4d$ resonances in Cu and Pd, respectively, and it is ~8 for the $3d$ one in Ni. If this model is right, the origin of thermal-induced entropy elasticity in $Pd_{40}Cu_{30}Ni_{10}P_{20}$ would not be the rotational and vibrational motions of polyhedral clusters,[7] but the locally collective atomic motion which corresponds to a hingelike motion between trigonal prismatic structure units connected by shearing edges.[8] The cooperative electron motion model was suggested long ago by Bloch[27] and Jensen,[28] but Hartree-Fock approximation had made this idea improbable in physical history. Recently, Mizubayashi *et al.*[29,30] have reported that anomalous elastic properties of amorphous alloys under anelastic strains are derived from a collective motion of many atoms. This is another expression of the cooperative electron motion.

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